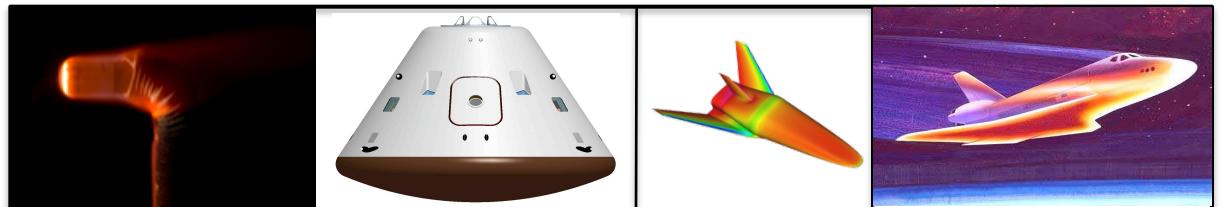




# Characterizing TPS Microstructure

## A Review of Some Techniques



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**NASA Ames Research Center**

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**ERC Inc**

### Acknowledgement

**David Gilley - Micromeritics Corporation**



# Outline

- Review of NASA Ames Capabilities
- Characterization Techniques
  - SEM
  - ASAP
- Summary



# Characterization Techniques - SEM

## Environmental Scanning Electron Microscope (ESEM)

- The XL30 ESEM combines a range of operating modes from high to low vacuum into a single versatile instrument, with different operating modes being easy to select and optimize to the particular application
  - Accelerating Voltage - 0.5 to 30kV
  - Magnification – 25x to 200,000x
  - Resolution ~5nm @ 30kV
  - Electron Backscatter Detector
  - Energy Dispersive X-Ray
- The XL30 ESEM located in TSM operates at chamber pressures up to 20 Torr
  - Allows a much broader range of materials to be imaged, particularly the many materials that contain water, or are of outgassing or non-conductive nature
  - Substantially reduces the need for specimen preparation (i.e. coating)

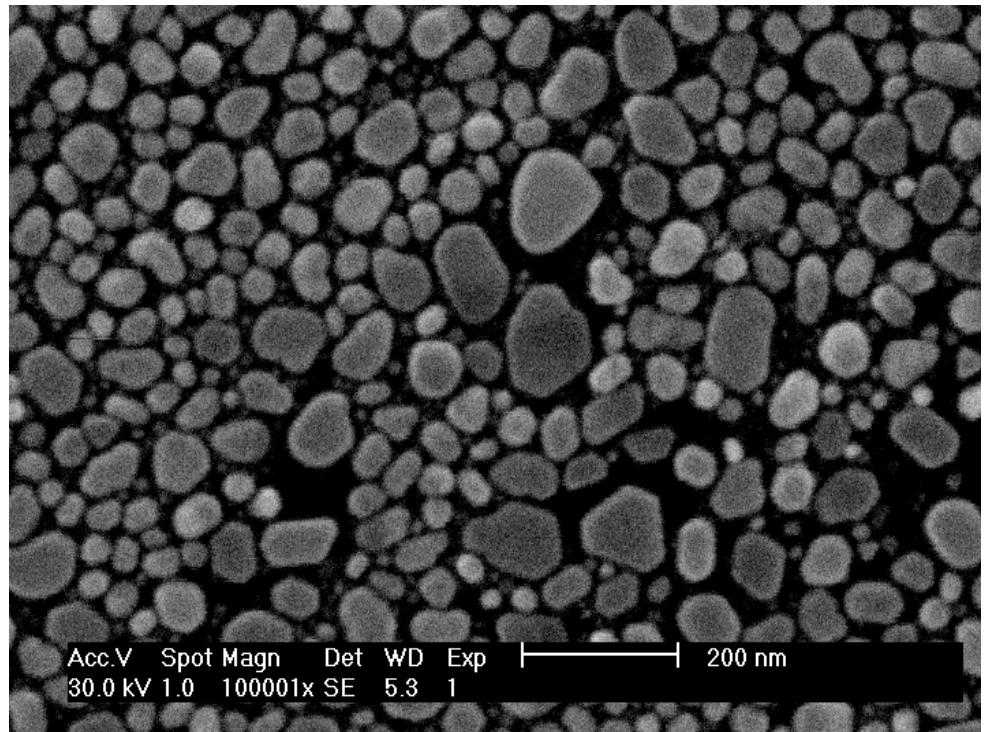




# SEM Resolution

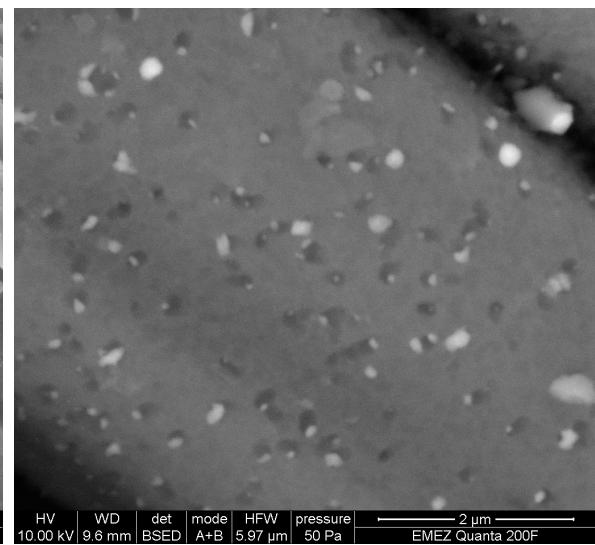
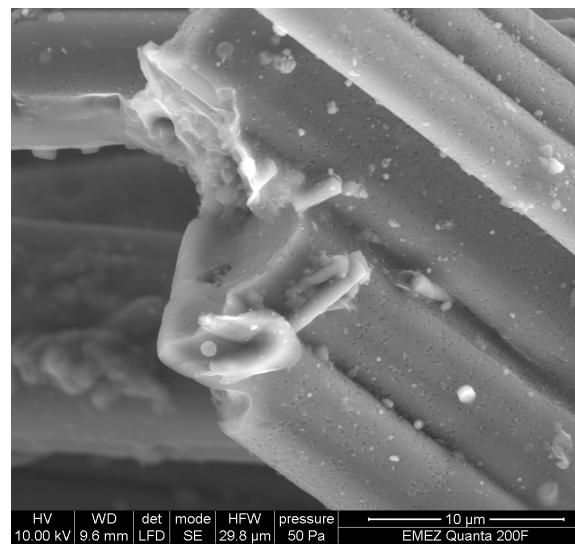
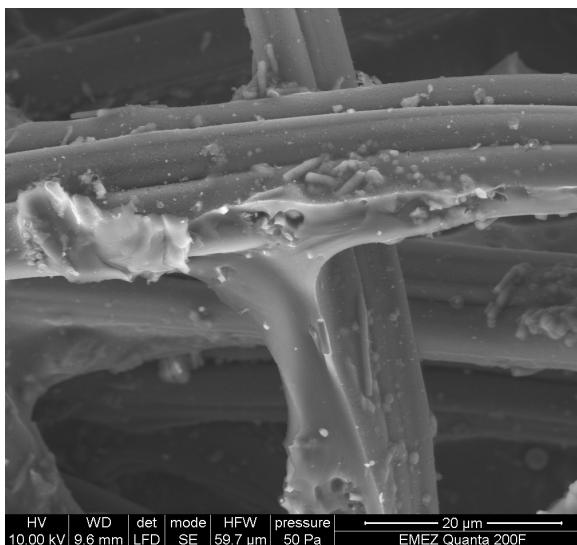
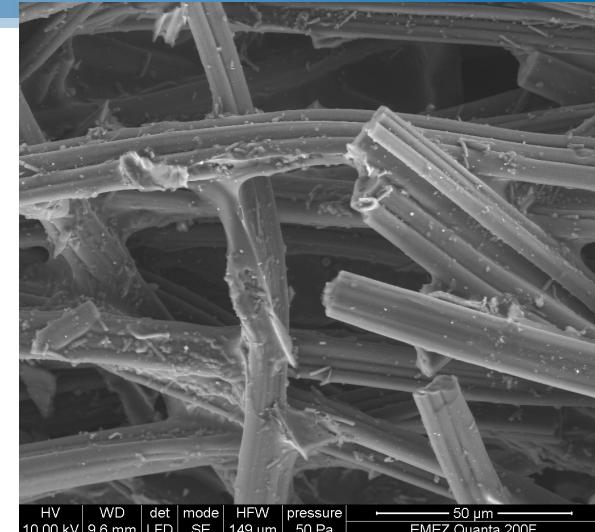
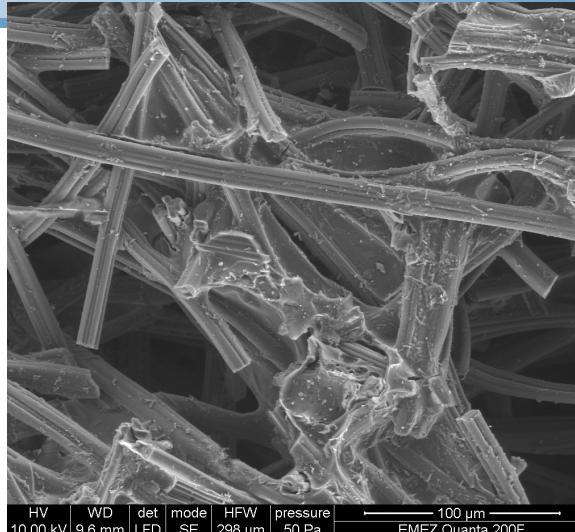
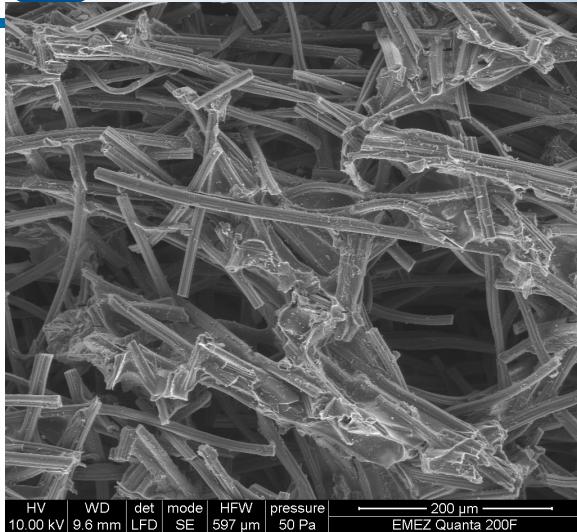
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# SEM of Rigid Carbon Substrate at Different Scales



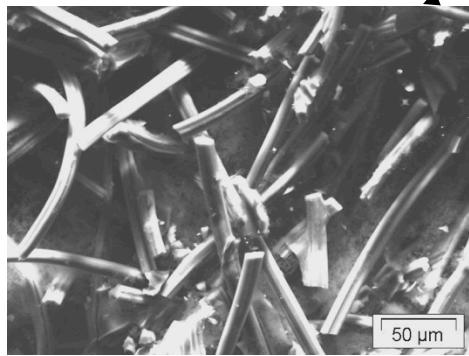
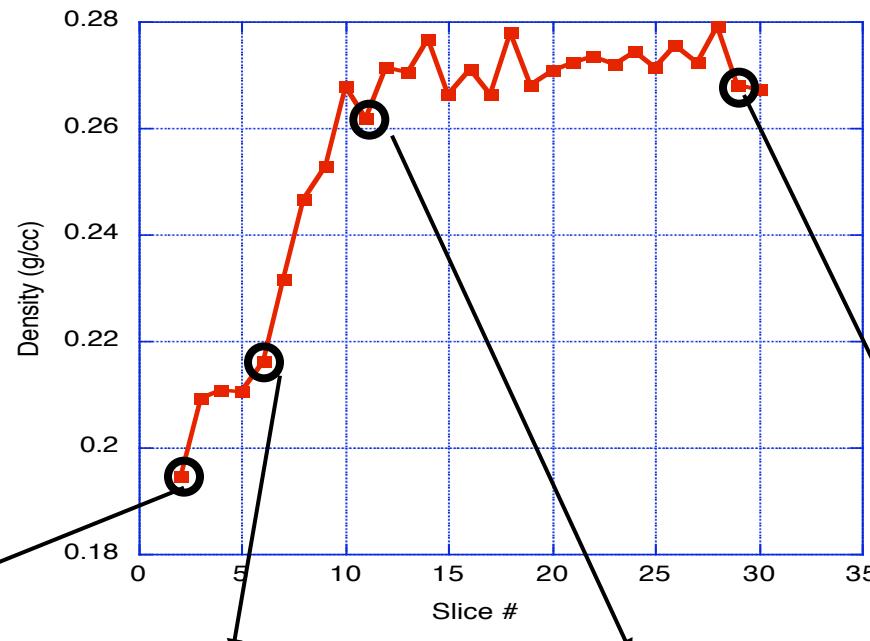
Highlights importance of high resolution SEM to capture fiber surface details which are not obvious at lower magnifications



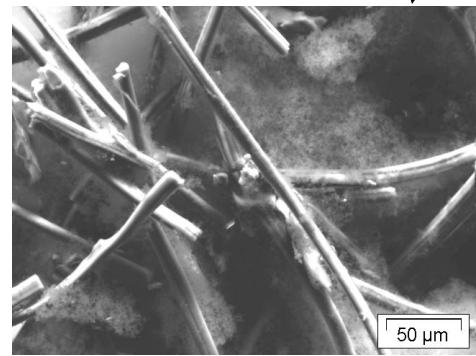
# Microstructure of Stardust PICA

Combined with other techniques SEM is a powerful tool to aid in explaining data

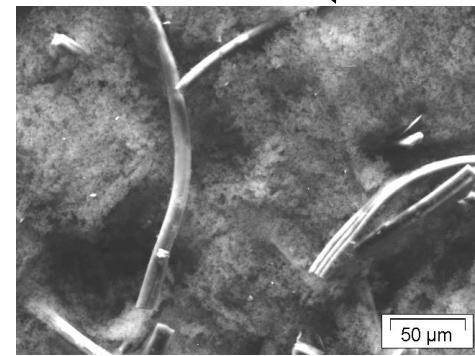
- Phenolic char high surface area phase is absent in slices 1 and 2
- Absence of phenolic char constituent accounts for density drop in first few millimeters of sample char surface



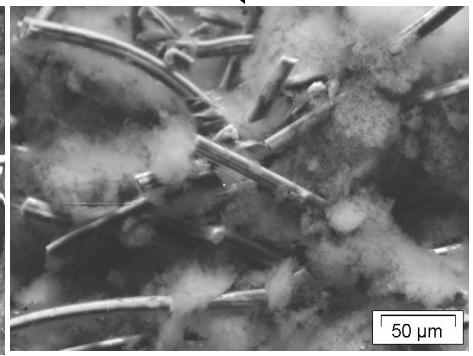
Slice 2



Slice 6



Slice 11



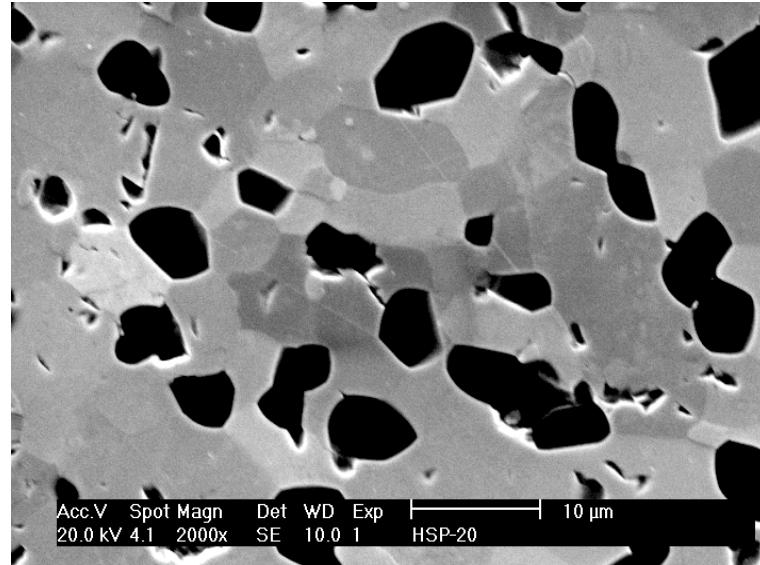
Slice 29



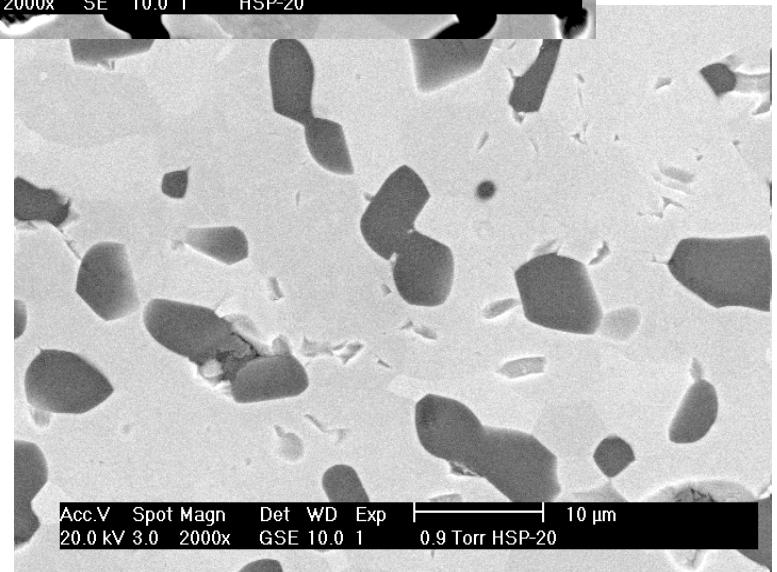
# SEM Backscatter Analysis

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SE Image



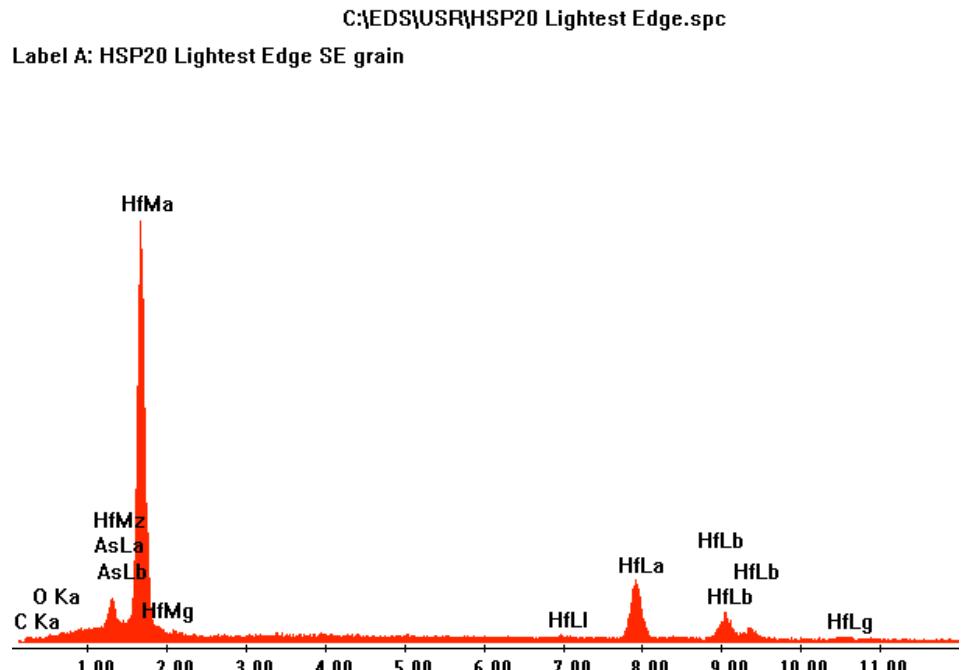
BSE Image



# SEM X-Ray Analysis

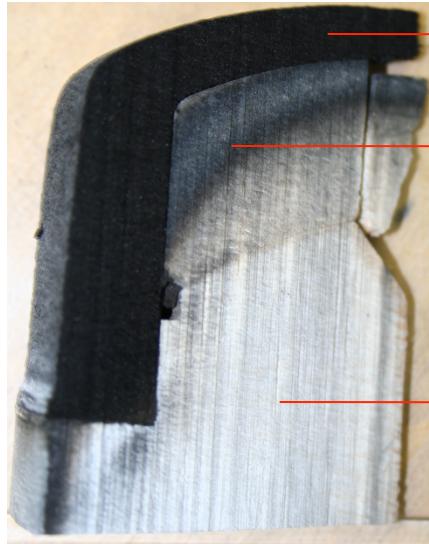
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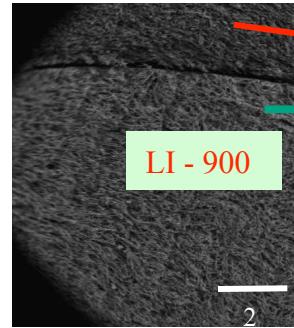


# SEM EDX Mapping

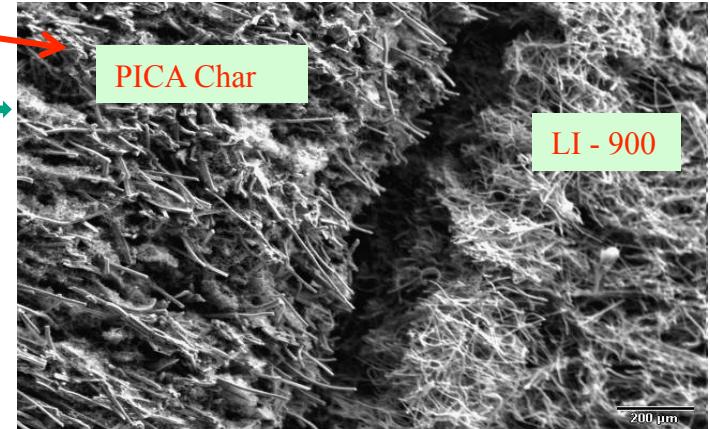


Charred PICA

LI-2200

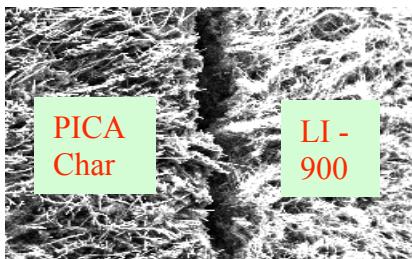


LI - 900

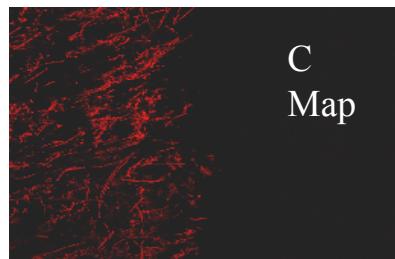


PICA Char

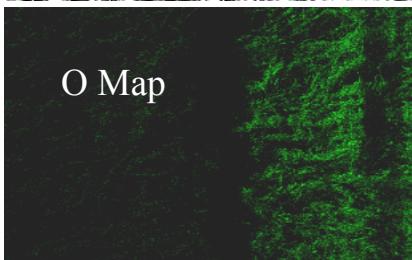
LI - 900



O Map



C  
Map



Si  
Map

- SEM systems comes with the X-ray detector that can perform the EDX analysis for upto 2 um depth.
- EDX analysis can be use to identify the elements for a given material and create elemental surface maps.

2. “Validation Testing of a New Dual Heat Pulse, Dual Layer Thermal Protection System Applicable to Human Mars Entry, Descent and Landing”, J.O. Arnold, E. Venkatapathy, Y.-K. Chen, S. Sepka, P. Agrawal, 10th AIAA/ASME Joint Thermophysics and Heat Transfer Conference, 28 June - 1 July 2010, Chicago, Illinois, pp 2010-5050



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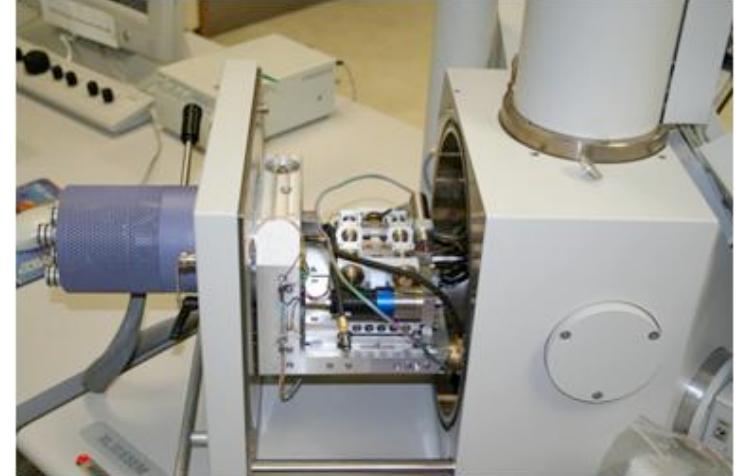
# In-Situ Electron Microscope Testing

## Objective

- Conduct thermal- mechanical tests on TPS materials and understand failure mechanisms at microstructural scale
- Use the understanding gained by these tests in materials process optimization and finite element modeling

## SEM - Stages

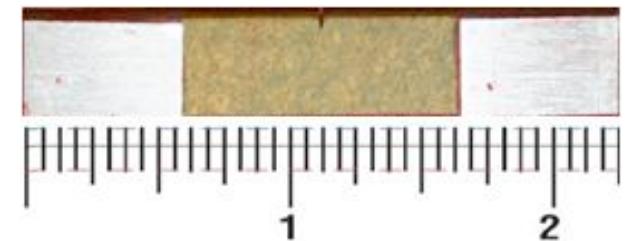
- Mechanical and thermal stages are mounted inside an environmental chamber as shown
- Uniaxial tension test, 3-pt, 4-pt bend tests can be performed on TPS material at room temperature, low (-400C) and elevated (1200 C) temperatures
- The stages are equipped with thermocouples and data acquisition system to monitor temperature and obtain stress-strain profile



Thermal/Mechanical stage  
mounted in SEM

## Baseline Tests for EDL Project

- Uniaxial tension tests are performed (at room temperature) on virgin and charred PICA material in the in-plane direction to establish baseline
- The coupons are notched at one end as shown in Figure 2 to focus the electron beam and observe failure mechanism
- Stress strain curves are obtained on both notched and un notched coupon to calculate fracture toughness and investigate the effect of discontinuity on overall behavior



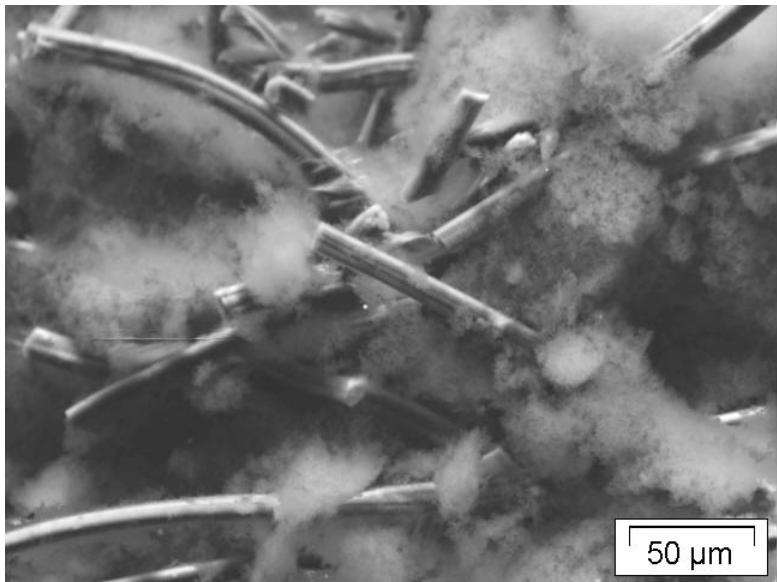
Notched PICA coupon



# Characterization Techniques - ASAP

## Accelerated Surface Area and Porosimetry System (ASAP)

- Atoms at the surface of a solid are incompletely bound. These surface atoms are more reactive and they attract gas (Van der Waals forces)
- Surface area is an important parameter in TPS (especially low density TPS)
- Surface area helps determine how
  - Solids oxidize
  - React with other materials



Example TPS with a very low density / high surface area phase



# Surface Area and Pore Volume

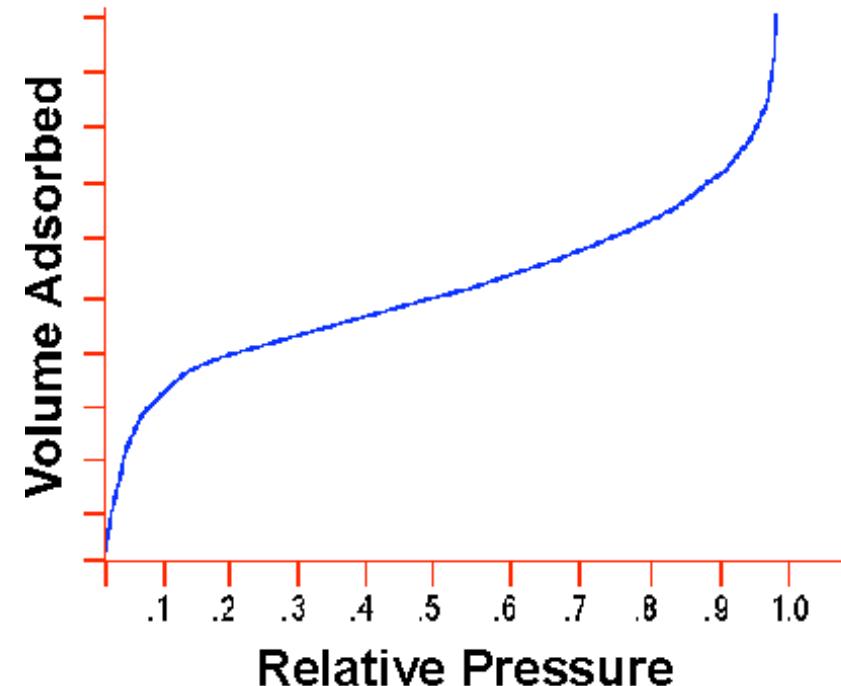
- Surface Area - Exposed extent of sample accessible to adsorptive
- Pore Volume - Volume of pores accessible to condensed adsorbate

## Types of Adsorption Isotherms

- The process of Adsorption is usually studied through plots known as adsorption isotherms
- Plot amounts of adsorbate gas adsorbed on the surface of sample at different pressures and constant temperature.

## Five different types of adsorption isotherm

- Depends on scale of porosity, adsorbate, sample, temperature etc



Type II Isotherm -  
Macroporous Samples



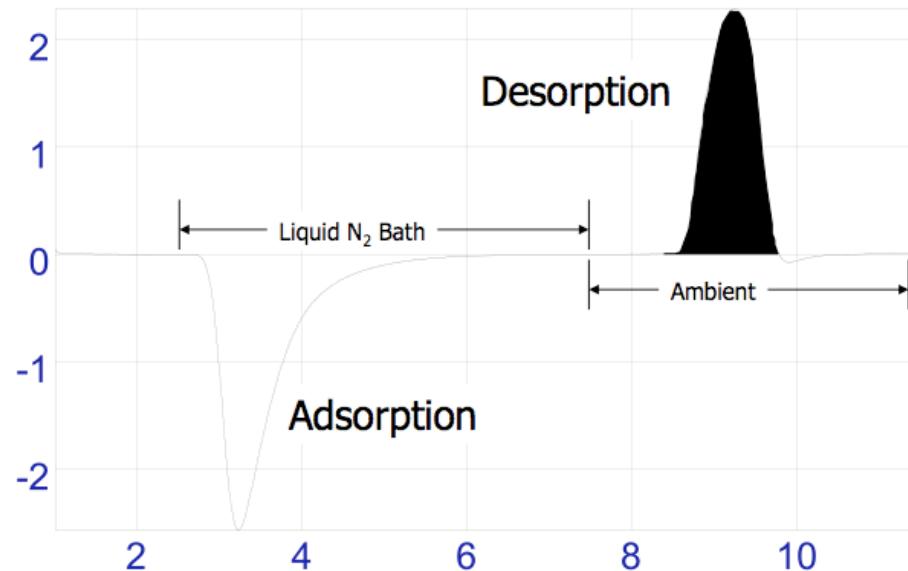
# Scale of Porosity (as defined by industry)

- Micropore - Less than 2 nm in size
- Mesopore - Between 2 and 50 nm in size
- Macropore - Greater than 50 nm in size



# Approach – Surface Area

- Sample preheated to remove adsorbed contaminants
- Sample cooled under vacuum to cryo temperature
- Adsorptive is introduced (usually N<sub>2</sub>) in controlled amounts
- Pressure allowed to equilibrate and the amount of gas adsorbed is determined for each amount of gas introduced
- Volume of gas adsorbed at each pressure gives an adsorption isotherm – from this isotherm the amount of gas required to form a monolayer over the solid external surface and its pores is determined
- Knowing the area covered by each adsorbed gas molecule the surface area can be calculated





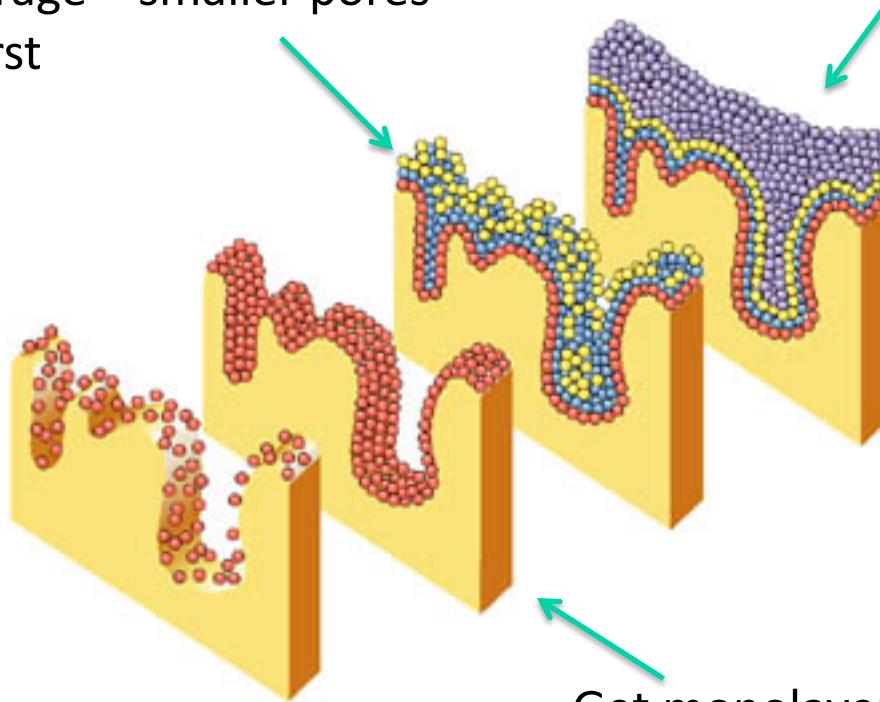
# Stages of Adsorption

Isolated sites on sample surface begin to adsorb gas at low pressures

Gas pressure is further increased resulting in beginning of multilayer coverage – smaller pores fill first

Get monolayer coverage as pressure increases (BET equation used to calculate SA)

Further increase in gas pressure results in complete coverage of sample and all pores filled – BJT calculation used to obtain pore diameter and distribution





# Approach – Pore Size and Distribution

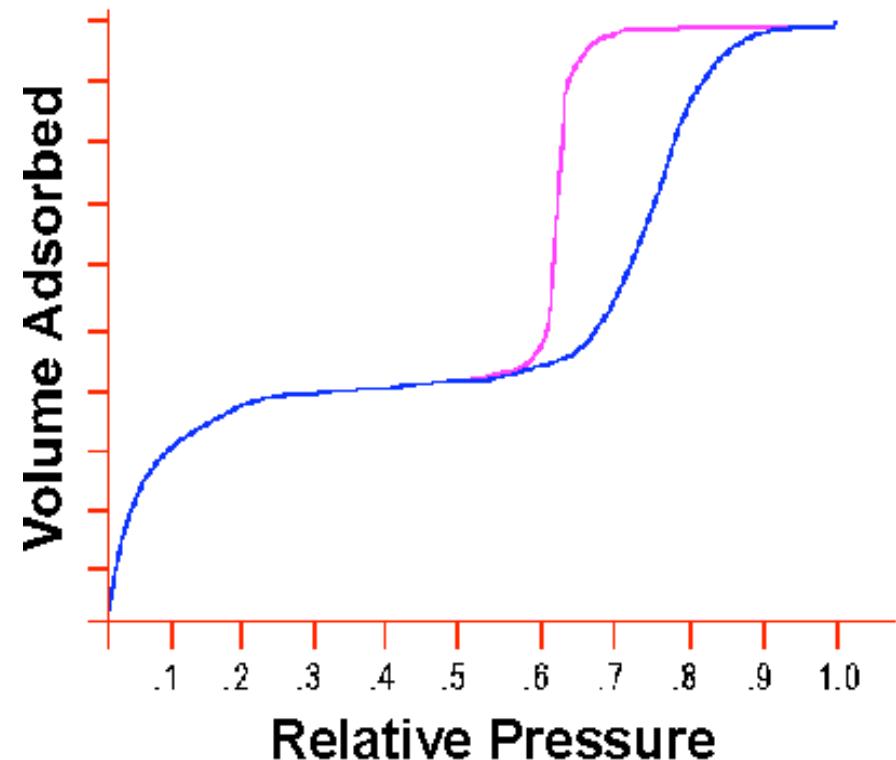
- When determining SA conditions to adsorb a monolayer of gas molecules on the sample are used
- The process can be extended to allow gas to condense in the pores and the fine pores in the sample can be determined.
- Increasing the pressure will cause gas to condense in the smallest pores initially
- Pressure is increased until saturation when the micropores are filled
- The pressure is then reduced in a controlled manner, evaporating the condensed gas
- The adsorption and desorption portions of the isotherm provides information on pore size and distribution
- Approach is only valid for very small pores



# Pore Size and Distribution

## Hysteresis

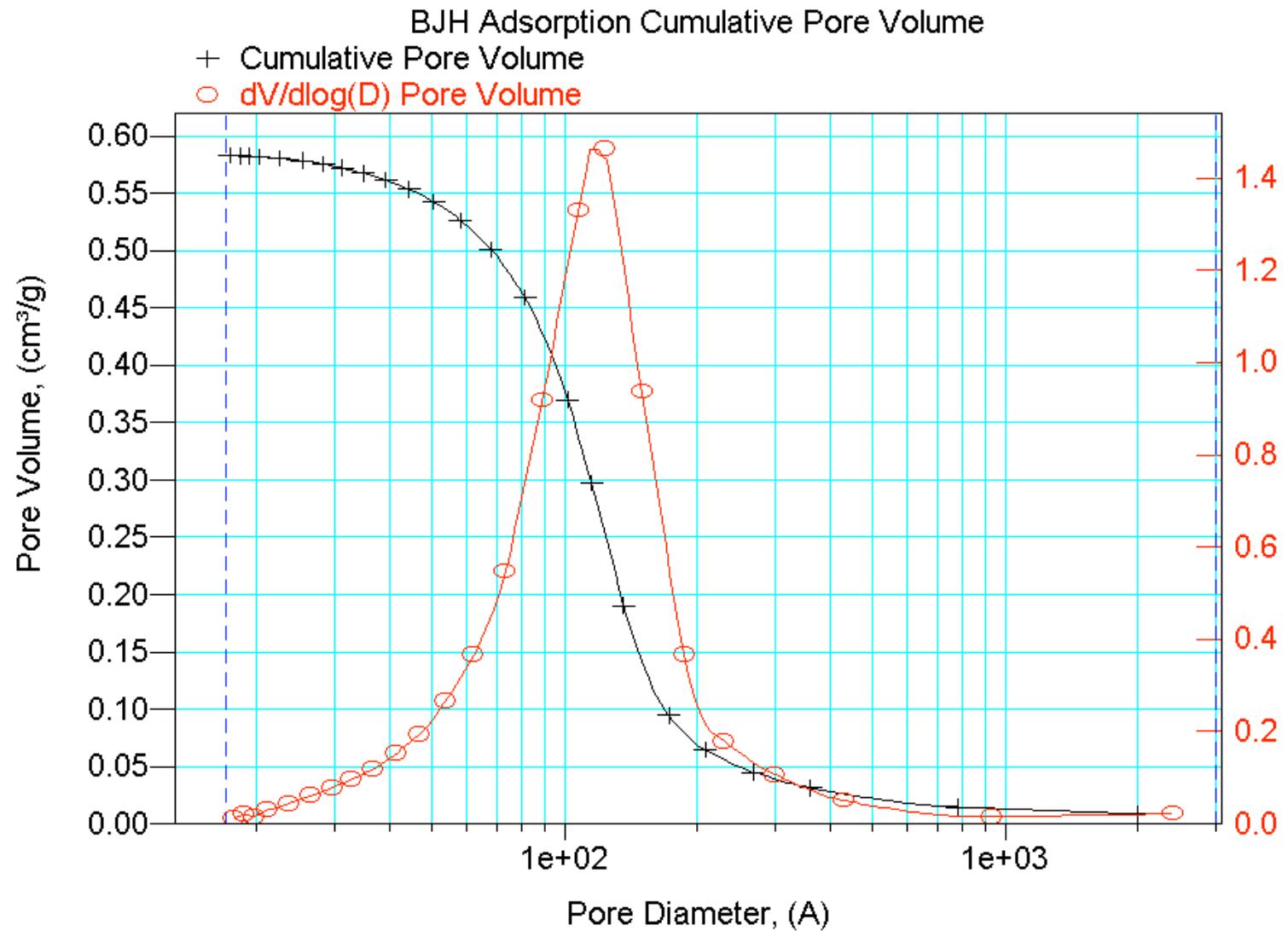
- Pores fill and empty at different relative pressures
- Originally used to describe pore shape
- Mostly due to connectivity of pores



Type IV Isotherm -  
Mesoporous Samples



## Example - Pore Volume Distribution of Silica-Alumina Catalyst Support





# Summary

- When seeking to understand ablator microstructure and morphology there are several useful techniques
  - SEM
    - Visual characterization at various length scales
    - Chemical mapping by backscatter or x-ray highlights areas of interest
    - Combined with other techniques (density, weight change, chemical analysis) SEM is a powerful tool to aid in explaining thermo/structural data
  - ASAP
    - Chemical characterization at various length scales
    - Chemical mapping of pore structure by gas adsorption
    - Provides a map of pore size vs. pore volume
    - Provided surface area of exposed TPS
- Both methods help characterize and understand how ablators react with other chemical species and provides insight into how they oxidize